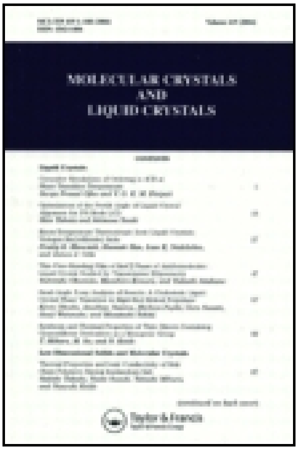

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Optical Second-Harmonic Generations of Liquid Crystalline Main-Chain Polymers and their Application for EO Devices

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The second harmonic generations (SHG) of liquid crystalline main-chain type polymers were investigated. The sample polymers are copolymers of 2-hydroxy-6-naphtoic acid (HNA) with 4-hydroxy-benzoic acid (PHB), in various composition ratios. SHGs for the samples by applying electric fields in some different manners at the liquid crystalline temperature were prepared. The nonlinear optical coefficients d_{exp} evaluated by Maker Fringe Method of electrically poled samples are 2–3 times larger than that of mechanically oriented sample whose d_{exp} is about 5pm/V. Quasi-Phase Matching (QPM) was performed by piling mechanically oriented thin films with alternatively directed machine direction. Using liquid crystals (nematic) as the spacer between films and surfaces and tuning refractive index of the liquid crystals by applying adequate electric field, SH intensity increased up to 12–15 times that of one sheet of film.

Keywords: liquid crystalline main-chain polymers; second-harmonic generation; mechanically oriented sample; piling thin films periodically inverted-polarized; Quasi-Phase Matching; liquid crystals

INTRODUCTION

Nonlinear optics (NLO) is still at the forefront of research because it is the key hardware technology for optical communication, signal processing and optical computing and so on. Several years have passed since optically nonlinear polymers were noticed as new kinds of the NLO materials. NLO polymers have advantages such as obtainable excellent thin films, their superior mechanical properties, and tailorability through chemical synthesis and processing[1-3]. In simplicity, NLO polymers can be divided into three categories: (1) the guest-host NLO polymers, (2) the side-chain type NLO polymers and (3) main-chain type NLO polymers. The first one can easily be obtained by blending the organic NLO materials with transparent polymers. The second one is to combine the NLO moiety to the main-chain polymers as the side-chains by chemical reactions or polymerization procedure. However, in these two, it has been pointed out that there exists a problem of orientational relaxation of NLO moiety[4,5]. The last one may be divided into two sub-categories: one is the NLO moiety combined in the main-chain as the component of the back bone and the other is the main-chain itself, showing large NLO properties.

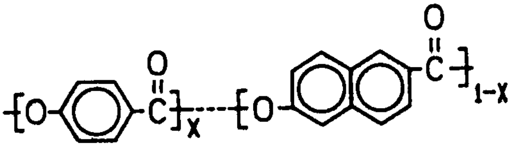
Some liquid crystalline polymers exhibit very large optical nonlinearities[6]. The molecular structure of the liquid crystal polymers is noncentrosymmetry, and the molecules are easily oriented to get solid structure with broken symmetry when they are processed in the liquid crystalline state. The advantages to use liquid crystalline main-chain polymer will be; (1) accumulation effect of individual units due to head to tail bonding, (2) spontaneous orientation of the chain molecules, (3) high stability (mechanically and thermally, etc.), (4) non-durability. Therefore, a study has been carried out to improve the second harmonic generation (SHG) of liquid crystalline main-chain polymers[6,7].

It has been reported previously[6,7] that the second order nonlinear optical coefficient (d_{33}) of the mechanically oriented films was above 10 x d_{11} that of the quartz. In this work, some trials of Quasi-Phase Matching (QPM) by making periodically inverted-polarization thin films will be introduced. Finally, a device for manipulating a lightwave will be proposed.

EXPERIMENT

Materials

The chemical structure of copolymers synthesized is as follows:



[PHB-HNA]$_n$

Copolymers of PHB and HNA in various molar ratios were prepared. The preparation of these wholly aromatic copolymers requires a melt condensation of 6-acetoxy-2-naphthoic acid with 4-acetoxy benzoic acid at high temperatures (Ca. 350°C) in N_2 atmosphere. The samples with a degree of polymerization (DP) around 30 were selected and used. The DP was evaluated by the ^{1}HNMR end-group method[8].

Preparation

The film samples obtained by a mechanical processing are called mechanically oriented samples, hereafter, and the orientation direction of the chain molecules is parallel to the machine direction.

The procedures used for electrically oriented samples are classified using (1) Sandwich cell type, E-1 sample, (2) Transverse cell type, E-2 sample, and (3) Corona-poling. The methods (1) and (2) have been reported previously [9].

(3) Corona poling: A traveling microscope was modified to be used as an adjustable electrode for corona poling, substituting microscope parts with electrode parts. A 2cm length tungsten wire was used as the plus electrode. The sample prepared by corona poling will be noted as E-3. The applied voltage, time and temperature will be described for individual specimen. 8kV, 18mm (between electrodes), at the liquid crystalline temperature 290°C, and 1 hour (application time) were most commonly used.

Measurement

The SHG of the film samples was generally evaluated by Maker Fringe

Method[10]. The Nd: YAG laser (Spectron, SL 401) was used as the light source (wavelength = 1064nm). The experimental apparatus for SHG measurements has been described previously[7]. The second harmonic NLO coefficient d_{33} of the films was evaluated by Maker Fringe Method, compared with standard Y-cut quartz d_{11}. In case it was difficult to use Maker Fringe Method to obtain d_{33} or d_{exp} for a film, they were evaluated by using Yariv's Equation[11] for conversion efficiency. SH efficiency and also conversion efficiency were evaluated by similar method that have been shown by Yariv[11]. An array detector was used instead of photographic plate. As a reference, the conversion efficiency of a well defined KTP crystal was measured and compared.

RESULTS AND DISCUSSION

Second Harmonic Generations of the Poled Samples

As reported previously[9], the d_{exp} evaluated of the film samples (E-1) and (E-2) are two or three times as large as that of mechanically oriented sample. d_{exp} (electrically oriented) $\cong$ 10-15pm/V.

To the contrary, the d_{exp} of the corona-poling sample is rather small than expected. At present, a value almost half as large as that of the above two electrically applied samples is obtained.

Second Harmonic Generations and Structure of the Mechanically Oriented Samples

Mechanically oriented sample films to be reported here were prepared as follows: The liquid crystalline polymer (LCP) was firstly molten into liquid crystalline state in the reservoir and then was instantly stretched in one way from the slit. This method is similar to a usual T-die extension but stretch is done only in one direction.

As reported previously[6,7,9], SH intensities are observed when the directions of electric vector of the incident light coincide with the direction of molecular long axis. The second nonlinear optical coefficient d_{33} of the mechanically oriented films is as large as 10 x d_{11} (quartz) measured by Maker Fringe Method.

Quasi-Phase Matching by Using Mechanically Oriented Samples

Though the electrically oriented samples show two or three times larger values for second nonlinear optical coefficient d_{33} , the area of the obtained film is very small. Moreover, smoothness of the surface of the films (E-2, E-3) are rather poor compared with that of mechanically oriented films. Consequently, at present, they are not said to be good nonlinear optical materials. To the contrary, mechanically oriented sample films can obtain large area at one time and the smoothness of the surface of the films is much better.

Consequently, a trial has been performed to utilize the mechanically oriented sample films for application devices.

It has been known that the alignment of periodically inverted-polarized domains can make quasi-phase matching and often shows high SH efficiency. Here, the quasi-phase matching was tested, using mechanically oriented samples.

As shown in Figure 1 schematically, a periodically inverted-polarized domain is easily obtained by piling the films so that the machine directions of the films change alternatively, keeping opposite directions with each other.

A system of 4 or 5 sheets improve the SH efficiency. When we add thin appropriate liquid crystal films between those oriented polymer films and on the surfaces, the SH efficiency increases more than 12-15 times than otherwise. The appropriate liquid crystal does mean that it has adequate refractive index matching with those polymer films.

The schematic picture of the device is shown in FIGURE 2. In this figure, the liquid crystal (Nematic) films are represented by thick solid line.

Application of Electric Field

When an adequate electric field is applied on the nematic liquid crystals which are between two sets of electrodes, the molecules align to one

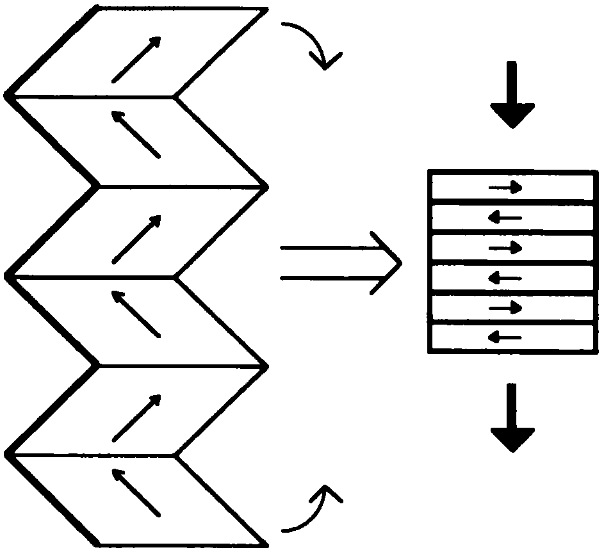


FIGURE 1 Schematic representations to make inverted - polarized piled films.

direction. For example, in the case of positive nematic liquid crystals, the molecules orient parallel to the electric field and the refractive index increases than otherwise.

In FIGURE 3 is shown a schematic picture of the device which can tun the refractive index of spacer liquid crystals and get much higher SH efficiency.

Thus we can control refractive index of spacer liquid crystals so as to coincide with that of NLO polymer films by adjusting the applied voltage. Once suitable electric field, which generate the most highest SH efficiency, applied the high SH efficiency hold to some extent even after the cessation of electric field application. After the cessation of electric field application, SH efficiency usually remain about 60(%) of the value during application of voltage. Consequently, we can control SH efficiency between these range

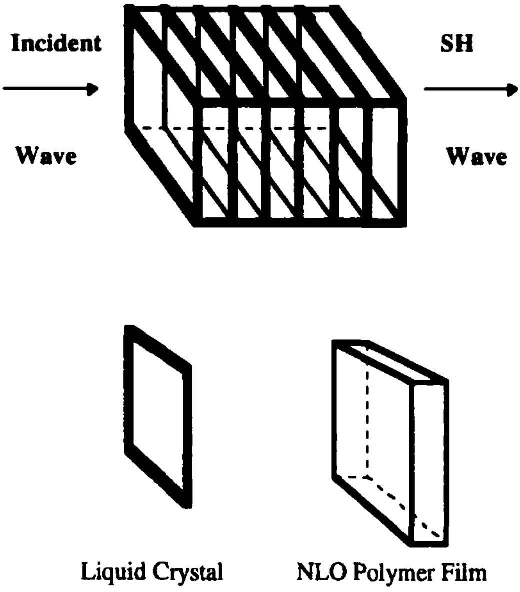


FIGURE 2 Schematic representation of the piled structure of NLO polymer films and liquid crystal films.

(from 60% to 100%). 100% does mean that the SH efficiency is 12-15times as large as that of one sheet of film. Conversion efficiency attained is nearly 26%. When the direction of electric field is varied by rotating the pair of the electrodes, the SH efficiency can be varied from 0 to 100% (=Maximum value).

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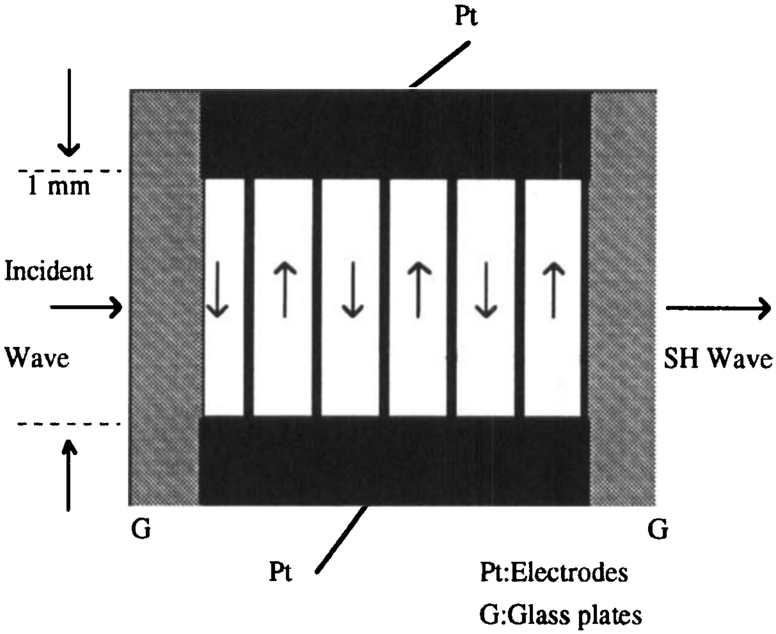

FIGURE 3 Schematic picture of the device which can tune the refractive index of spacer liquid crystals by electric field application.

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